Design of Coal Liquefaction Catalysts with Functions for Recovery and Repeated Use

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Abstract

Active catalysts with functions for recovery and repeated use are expected to reduce the cost and waste in the coal liquefaction. The authors are going to propose basically two types of catalysts which are recoverable for the repeated use. The first type is acid-proof iron catalysts which are recoverable from the mixture with carbonate and chloride minerals. Such catalysts are applicable to particular coals such as Australian brown coal which is completely liquefied, carrying calcium and magnesium carbonates as the major minerals after the primary liquefaction.

Second type is characterized by its sulfur-proof ferromagnetism for the recovery from the minerals and carbons by gradient magnetic field. The authors are going to describe the performances of Fe_3Al powder and carbon-coated ferrite. Fine powders are essential for their high activity.

The deactivation of the catalyst by carbon and minerals in the liquefaction should be clarified, and a multi-step liquefaction scheme including coal pretreatment can be designed to minimize the deactivation.

Introduction

Coal liquefaction has been rather extensively investigated for longer than several decades to provide clean liquid fuel from coal in order to meet the increasing demand expected in early next century. However the cost of the liquid fuel is still too high to substitute the fuel from petroleum. Several break-through ideas are strongly wanted to cut the cost currently estimated.

Cut of installation cost appears most effective. The ways are
1) More moderate conditions

2) Better yields per installation, more change of coal and better conversion
3) Simpler scheme,
       1.hydrogen source
       2.solid-liquid separation
4) Stable operation for years
5) Cheaper catalyst and residue handling

       The present authors have been studying a complete conversion of coal (no organic residue), with least amount of hydrogen donor in the reactor by multi-stage scheme which includes the coal pretreatment, coal dissolution, catalytic up-grading. The catalyst of primary liquefaction stage is a key to be developed. The authors assumed that the recovery and recycle of the catalyst from the residue is as approach to reach the objective described above.
       In the present report, recovery and recycle of the catalyst for the primary liquefaction stage were studied .The basic idea is to recover the catalyst from the inorganic residues which come from the feed coal. According to the natures of inorganic residue, two approaches were examined in the present study.
   1.Washing out the inorganic residues such as carbonates which are principally found in Australian brown coal
   2.Recovery of the ferromagnetic catalyst from the diamagnetic residue by applying the magnetic gradient.
       The catalyst deactivation and adhesion of the catalyst and minerals should be avoided by designing the scheme. The pretreatment and hydrogen transferring liquefaction as the prior to the catalytic steps are responsible.The catalyst and organic residue can be recycled to the liquefaction stage when the organic residue still carries significant amount of reactive portions.

Experimental
Materials
       The liquefaction (hydrogen donating) solvent was a hydrogenated fluoranthene prepared by catalytic hydrogenation of commercial fluoranthene (FL) using a commercial Ni-Mo catalyst in an autoclave at $250\,°C$, under initial hydrogen pressure of 13.5 MPa. The major component of the solvent was 1,2,3,10b-tetrahydrofluoranthene (4HFL),

which was identified by ^{1}H and ^{13}C n.m.r., quantified by g.c., and purified by recrystallization with n-hexane, removing perhydrofluoranthenes (PHFL).

Liquefaction procedure

Liquefaction was carried out in an autoclave (50ml volume). The ground coal (3.0g), the solvent (4.5g) and catalyst (0.9g) were transferred to the autoclave. The products remaining in the autoclave were extracted with THF, benzene and hexane.The hexane soluble (HS), hexane insoluble but benzene soluble (HI-BS), benzene insoluble but THF soluble (BI-THFS), and THF insoluble (THFI) substances were defined as oil, asphaltene, preasphaltene, and residue, respectively. A small amount (<5%) of solvent derived products, which remained in the HI-BS fraction, was corrected by g.c. analysis. The gas yield was calculated by the difference between the initial (dry ash free base) and recovered residual weights. Thus, the weight loss during the experiment was included in the gas yield.

Hydrogenation of 1-MN procedure

Hydrogenation of 1-MN was carried out in an autoclave (50ml volume). 1-Methylnaphthalene (1.0g), Decahydronaphthalene (9.0g) and catalyst(0.3g) were transferred to the autoclave. The reaction products were washed out with acetone. Hydrogenation conversion and products were determined with GC and GC-MS , respectively.

Results

Catalytic activity of washed residue in the liquefaction of Australian brown coal.

Figure 1 summarizes the catalytic activity of the residue in the solvent washing, and ones resulfided, S-added or washed followed by resulfiding in the liquefaction of the brown coal. Basically the residues indicated similar activities, although the resulfiding enhanced activity to produce more gases. The point is that the washing removed almost completely the inorganic carbonates, concentrating the ion catalyst. Thus, the bottom recycle can be performed by avoiding the accumulation of the inorganic residues. Even if the catalyst is covered by the carbonates, such washing can remove the carbonates without diferiolating the catalytic performances.

Ferromagnetic catalysts

Two kinds of ferromagnetic catalysts are examined in the present study, Fe3Al and carbon-magnetite composite. Their catalytic activities are illustrated in Figure 2. Both of them exhibited significant activities and maintained ferromagnetic susceptibility after the liquefaction. Their susceptibility stood in H_2-H_2S atmosphere at 400 ℃.

Ferromagnetic support

Table 1 shows the activity of NiMo supported on Fe3Al for the hydrogenation of 1-methylnaphthalene at 380℃ for 40min under H_2 pressure of 10MPa ; Non-trivial activities were induced by supporting NiMo on Fe3Al. The catalyst maintained the ferromagnetic susceptibility.

Discussion

The present study indicated that the recovery and recycle of the catalyst are basically possible after the primary coal liquefaction where the inorganic residues are present to contaminate the iron catalyst. Although the catalytic activity so far revealed is not super yet, more elaborate preparation of the catalyst can improve the activity without losing functions of recovery. Smaller particle size, better dispersion and favorable catalyst-support interaction are applicable ways to enhance the activity.

The reaction scheme including coal pretreatment procedure should be also examined for further development to avoid the catalytic deactivation.
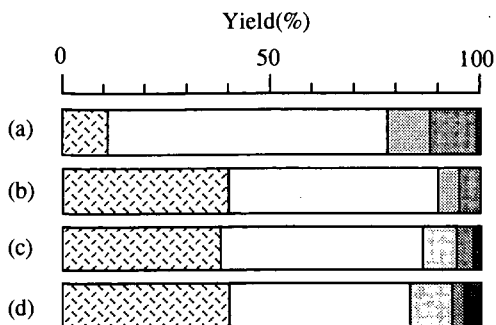
Yield(%)

Fig.1 Effects of pretreatment for several recoverable catalyst to the liquefaction yields

catalyst: 3% addition to coal
solvent(75%4HFL/25% Py)/ coal= 1.5
single-stage used autoclave
380℃-40min,H2Press.10MPa

(a) ; non-treatment Y-coal PI
(b) ; presulfided   Y-coal PI
(c) ; presulfided and S-additon Y-coal PI
(d) ; acetic acid washing and
       presulfided Y-coal PI

☒ :G   □ :O   ▦ :A   ▦ :P   ■ :R
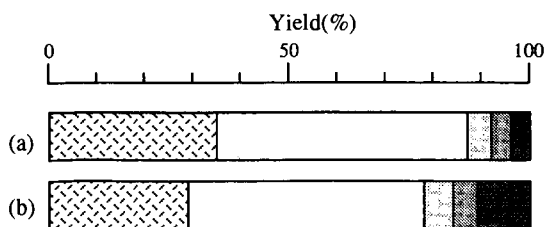
Yield(%)

Fig.2 Effects of Fe3Al catalyst
         to the liquefaction yields

catalyst: 3% addition to coal
solvent(75%4HFL/25% Py)/ coal= 1.5
single-stage used autoclave
380℃-40min,H2Press.10MPa

(a) ; C/Coated Magnetite, (b) ; Fe3Al

☒ :G   □ :O   ▦ :A   ▦ :P   ■ :R

97

Table 1   Catalysttype and 1-MN hydrogenating conversion

Catalyst (NiMo/Fe₃Al)	Mo wt%	Ni wt%	Conversion %
A	10	2	9
B	10	5	13
C	5	1	5
D	10	5	20
E	10	5	23

Sulfiding conditions (ABC:360℃ 6hr   D: 300 ℃   3hr
E: 360 ℃ 3hr after   300 ℃   3hr)
Reaction conditions (1-MN:1.0g DHN:9.0g
catalyst:0.3g   used autoclave
380℃-40miin,H₂press.10Mpa.

98

THE EFFECT OF CATALYST DISPERSION ON
COAL LIQUEFACTION WITH IRON CATALYSTS

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INTRODUCTION

Dispersed catalysts have been used for first stage direct coal liquefaction studies. Compared to supported catalysts, dispersed catalysts offer many advantages for first-stage coal liquefaction, such as the lack of aging and, for inexpensive catalysts, such as iron, the ability to simply dispose of the catalysts. The effectiveness of dispersed catalysts depends on the dispersion of the catalyst in the coal-vehicle system. Catalyst dispersion can potentially be improved by two methods in coal/catalyst systems: improving contact between coal and catalyst during the initial stages of coal liquefaction and optimizing the physical properties of the catalyst, i.e. increased surface area, smaller particle size, or smaller crystallite size.

Dispersion is usually treated qualitatively. Studies have shown that methods of catalyst preparation that should result in enhanced levels of catalyst dispersion also result in the highest levels of catalyst activities as measured by coal conversion to soluble or distillable products.[1-7] Methods of enhancing catalyst dispersion which have been investigated include developing techniques to increase the surface areas and/or reduce the particle sizes of catalysts, using aqueous catalyst impregnation of coal, and coupling aqueous impregnation with coal swelling.

Enhancing catalyst dispersion has been found to be effective with iron systems. It has been reported that the effectiveness of iron catalysts can be improved by decreasing their initial particle size.[8-10] However, sintering or agglomeration has been observed under liquefaction conditions.[11-14] Coal as well as sulfate pretreatments can act to mitigate this effect.[13-15]

Another means of enhancing the activity obtained with iron catalysts is to improve the contacting between the coal and catalyst. Workers have attempted to use forms of iron catalyst precursors that are soluble in oil or aqueous media. The solubilized precursor could then either be precipitated onto the coal's surface prior to charging the reactor or directly mixed with the coal/solvent mixture in the reaction. Studies have shown that

catalyst pretreatments that result in enhanced levels of contacting between coal and catalyst also result in higher levels of coal conversion.[3,16 and 17]

Recent work at PETC has centered on the development of an iron catalyst precursor that is intimately contacted with the coal and maintains a fine particle size upon conversion to the active, sulfided phase. The procedure, reported previously,[3] results in the precipitation of FeOOH directly on the coal surface. Failure to intimately contact the FeOOH with the coal surface resulted in the loss of iron activity. The present study investigates the surface area and particle size changes resulting from the transformation of the precursor, FeOOH, to the active phase, presumably pyrrhotite. The effect of improved contacting between the FeOOH and coal was also investigated.

EXPERIMENTAL

Experiments were conducted with Blind Canyon bituminous (DECS-6, from the DOE/Penn State Coal Sample Bank) and Black Thunder subbituminous coals. Properties of the feed coals are presented in Table 1.

The catalyst precursor was added to the reactor as a dry powder, aqueous solution or by precipitation onto the coal. Hydrated iron oxide (FeOOH) was dispersed onto the feed coals by an incipient wetness impregnation/precipitation approach.[3] Forms of iron tested include powdered Fe_2O_3, aqueous ferric nitrate, aqueous ferrous sulfate, and powdered FeOOH. A sample of Fe_2O_3, with a nominal particle size of 1μ (from Spang and Company) was added as a dry powder. High surface area, powdered FeOOH was prepared by precipitating FeOOH from an aqueous solution of ferric nitrate by the addition of ammonium hydroxide. The precipitate was recovered by filtration through a 0.45μ filter, was vacuum dried at 40°C, and ground to a powder. The N_2 BET surface area of the FeOOH prepared in this manner was 138 m^2/g. Catalyst prepared in this way was added to the reactor in a physical mixture with the coal.

The effectiveness of each catalyst precursor was determined by using each precursor in a 40-mL tubular microautoclave reactor. Experiments were conducted by adding 3.3 g coal to the reactor with 6.6 g of Panasol (a mixture of alkylated naphthalenes obtained from Crowley Chemical). Elemental sulfur (0.1 g) was added to the reactor to sulfide the catalyst precursors. The reactor was charged with 1000 psig (6.9 MPa) of hydrogen and sealed. The pressurized reactor was then heated to the liquefaction temperature in a fluidized sandbath. The heating period lasted 30-40 minutes. Following the liquefaction period (0.5 h), the reactor was cooled and depressurized. Coal conversion was calculated from the solubility of the coal-derived products in THF and in heptane as determined by a pressure filtration technique.[18]

Microautoclaves were also employed to investigate the transition of impregnated FeOOH to pyrrhotite. In these

experiments, FeOOH was impregnated onto carbon black rather than coal to eliminate interferences on subsequent analyses from the indigenous pyrite in the coal. The carbon black was Raven 22 Powder obtained from Columbian Chemicals Co. The iron-loaded carbon black and tetralin were heated (under H_2 in the presence of CS_2) to 400°C and held at temperature for 5 minutes. The products were mixed with THF and filtered through a 0.45μ filter. The filter cake, containing the iron loaded carbon, was recovered and analyzed by X-ray diffraction (XRD).

A series of iron sulfide catalysts (pyrrhotite, as analyzed by XRD) were prepared from the iron oxide precursors as well as from aqueous ferric nitrate solution and aqueous ferrous sulfate solution. The iron sulfide was prepared by adding the precursor to a 1-L autoclave containing tetralin. The mixture contained 400 g of tetralin and sufficient precursor to produce 4 g of iron sulfide. To convert the precursor to catalyst, the mixture was heated to 400°C and held for 0.5 h under 2500 psig (17.3 MPa) of $H_2/3\%H_2S$ which was passed through the reactor at 4 SCFH. The recovered iron sulfide catalysts were extracted with THF.

RESULTS AND DISCUSSION

Catalyst Surface Area

The effect of iron oxide surface area was investigated using powdered FeOOH with a surface area of 138 m^2/g and micronized Fe_2O_3 with a surface area of 5 m^2/g. Table 2 gives the effect of precursor surface area (iron oxide) on coal conversion. The precursor surface area does not appear to be important. This was expected to some extent since the precursor undergoes a chemical reaction to form the catalyst. The surface area of the catalyst itself is the important variable. Consequently, a series of tests were conducted to determine the relationship between the surface area of the catalyst (pyrrhotite) and the surface area of the original iron oxide. The catalyst was formed from the precursor in tetralin with an H_2/H_2S atmosphere as described in the experimental section. XRD and BET surface area were conducted on the resulting pyrrhotite. Table 3 presents the surface areas and crystallite sizes of the resulting iron sulfides (pyrrhotites). Also shown in Table 3 are the characteristics of pyrrhotites resulting from soluble iron precursors (ferric nitrate and ferrous sulfate). The analyses showed that the pyrrhotite was crystalline with estimated crystallite sizes ranging from 42 to 82 nm by XRD. The BET surface area analysis indicated that the surface area of the resulting pyrrhotite was significantly different than that of the original iron oxide. For the high surface area precursor, the surface area dropped from 138 m^2/g to 17 m^2/g, while the low surface area precursor increased its surface area from 6 m^2/g to 9 m^2/g. The similarity of the surface areas of the pyrrhotites resulting from the solid iron oxide precursors helps to explain the similar coal conversions observed with each. The surface areas of the pyrrhotites prepared by aqueous precipitation were both about 30 m^2/g, which is greater than those from either of the iron oxide

101

precursors.

The next series of tests conducted was aimed at investigating the effect of pyrrhotite surface area on coal conversion. Table 4 presents coal conversion as a function of iron sulfide surface area and crystallite size. It appears that there is a relationship between surface area and coal conversion. Clearly the precipitated precursors produced a higher surface area pyrrhotite and subsequently higher coal conversions.

Impregnation

The effectiveness of catalysts formed from FeOOH depends on the method by which FeOOH is added to the system. Table 5 compares coal conversion using physically mixed FeOOH with impregnated FeOOH. The impregnated FeOOH is more active and results in higher coal conversion than the physically mixed FeOOH. As shown in Table 3, the surface area of the iron sulfide formed from powdered FeOOH (not impregnated) in tetralin dropped to 17 m^2/g compared to 138 m^2/g for its precursor. This large reduction in surface area produced a catalyst which resulted in lower coal conversions compared to the conversions obtained when the precursor was precipitated onto the coal.

The surface area and crystallite size for the catalyst precipitated onto the coal may not be the same as those measured for the catalysts formed in pure tetralin. The pyrrhotite formed from coal-impregnated FeOOH is not easily characterized because of the presence of pyrite and other crystalline material in the coal. Therefore, a separate preparation of impregnated carbon black was prepared in order to see what effect impregnation has on crystallite size. The impregnated carbon black was subjected to liquefaction conditions and recovered by THF extraction. XRD analysis of the iron sulfide on the carbon black revealed that the average crystallite size of the catalyst was 27 nm. This is significantly lower than the pyrrhotite crystallite size formed from powdered FeOOH (56 nm). One of the effects of impregnation of the FeOOH appeared to be the generation of smaller iron sulfide particles in the system.

CONCLUSIONS

In the absence of a carbonaceous support, the transformation of FeOOH to iron sulfide results in a loss of surface area, possibly due to sintering. This effect has been previously documented.[11-14] The loss in surface area prevents a correlation between precursor surface area and coal conversion from being established. However, an increase in the surface area of the actual (iron sulfide) catalyst does appear to improve liquefaction yields. Iron sulfide preparations with a broader range of surface area need to be investigated.

The presence of a carbonaceous support for FeOOH tends to mitigate the sintering and favors the formation of smaller particle

size iron sulfide catalysts which are likely to have higher specific surface areas. It is likely that the same effect occurs in coal impregnated with FeOOH since addition of the precursor through impregnation results in higher coal conversions. However, the better contacting between coal and catalyst achieved by impregnation may also contribute to the higher conversions.

ACKNOWLEDGEMENTS

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Table 1. Analyses of Coal Feeds

	Black Thunder	Blind Canyon DECS-6
Proximate Analysis (wt%, as received)		
Moisture	19.2	4.7
Volatile Matter	34.8	42.4
Fixed Carbon	40.6	47.3
Ash	5.4	5.6
Ultimate Analysis (wt%, Moisture Free)		
Carbon	68.2	76.5
Hydrogen	4.8	5.9
Nitrogen	1.0	1.5
Sulfur	0.4	0.4
Oxygen (Difference)	18.8	9.9
Ash	6.8	5.8
Sulfur Forms (wt%)		
Sulfate	0.02	0.01
Pyritic	0.04	0.02
Organic	0.30	0.41

Table 2. Effect of Iron Precursor Surface Area on Coal Conversion of DECS-6 Blind Canyon Coal at 425°C, 0.5 h, 1000 psig (cold) H_2, 5000 ppm Fe, 0.1 g S added to 9.9 g of a 2:1 mixture of Panasol to DECS-6 Coal.

Precursor	Precursor Surface Area, m^2/g	Coal Conversion(%) To: THF Sols.	Heptane Sols.
None	None	58	30
FeOOH	138	66	34
Fe_2O_3	6	73	35

Table 3. Effect of Precursor Type and Surface Area on the Resulting Iron Sulfide Crystallite Size and Surface Area Produced in a 1-L Autoclave at 400°C, 0.5 h, 2500 psig $H_2/3\%H_2S$.

Catalyst Precursor	Surface Area m^2/g	Iron Sulfide Crystallite Size, nm @ $2\theta=53.2$	Iron Sulfide Surface Area m^2/g
Micronized Fe_2O_3	6	82.0	9
FeOOH	138	56.0	17
Aqueous Ferric Nitrate	n/a	43.0	30
Aqueous Ferrous Sulfate	n/a	42.1[1]	32

[1] Calculated based on surface area.

Table 4. Effect of Iron Sulfide Precursor Surface Area and Crystallite Size on Coal Conversion of DECS-6 Blind Canyon Coal at 425°C, 0.5 h, 1000 psig (cold) H_2, 5000 ppm Fe, 0.1 g S added to 9.9 g of a 2:1 mixture of Panasol to DECS-6 Coal.

Precursor Surface Area, m^2/g	Crystallite Size, nm @ $2\theta=53.2$	Coal Conversion(%) To: THF Sols.	Heptane Sols.
None	na	58	30
9	82.0	73	31
17	56.0	70	31
30	43.0	84	38
32	42.1[1]	76	35

[1] Calculated based on surface area.

Table 5. Effect of FeOOH Mode of Addition on Coal Conversion of
          DECS-6 Blind Canyon Coal and Black Thunder Coal at 425°C,
          0.5 h, 1000 psig (cold) H_2, 5000 ppm Fe, 0.1 g S added to
          9.9 g of a 2:1 mixture of Panasol to Coal.

Precursor	Coal Conversion(%) To:	
	THF Sols.	Heptane Sols.
Blind Canyon		
None	58	30
Physically Mixed FeOOH	66	34
Impregnated FeOOH	85	41
Black Thunder		
None	54	30
Physically Mixed FeOOH	64	35
Impregnated FeOOH	73	33

A STUDY OF DISPERSED IRON-BASED ADDITIVES
IN COAL LIQUEFACTION

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INTRODUCTION

Iron-based additives have been extensively (1-5) evaluated for their catalytic behavior in direct coal liquefaction. The catalytic activity of these iron-based additives depends not only on their chemical composition but also on their effective contact area with the coal/solvent mixture. Various preparation techniques have been investigated (6) to produce nanoscale iron-based catalyst precursors to enhance its activities.

The activity of two different iron-based additives for liquefying a Wyoming sub-bituminous coal, Black Thunder mine coal, was evaluated in a two-stage, bench scale continuous flow unit. One of these additives, iron oxide, was introduced in form of a powder to the slurry feeding system, while the second additive was impregnated on the coal matrix using an incipient wetness technique developed at the Pittsburgh Energy Technology Center.

This paper describes the findings of the bench scale evaluations (Runs CC-7 and CC-15) which were intended to examine the relative effects of catalyst type and reactor configuration (e.g. Catalytic/Thermal or Thermal/Catalyst).

EXPERIMENTAL

Coal Preparation

Black Thunder mine coal was used as feed. Analyses of the feed coals are shown in *Table 1*. The feed coals (HRI-5630 and 5828) were screened to -70 mesh and dried under nitrogen to obtain moisture content between 5-10 W% for tests when the iron additive was added in form of a powder. The impregnated coal feed (L-780) was dried to 5 to 12 W% moisture content.

The PETC incipient wetness technique involves the contact of coal with a solution of iron salt followed by precipitation (impregnation) of hydrated iron oxide on accessible coal surfaces.

The iron content of the untreated coal was 0.2 W% (dry basis), while that of the impregnated coal feed contained 0.57 to 0.65 W% of iron.

Start-up/Make-up Solvent

Each run was start-up with coal derived distillates. The start-up oil used in CC-7 was HRI-5648 and was derived from Wilsonville using Illinois coal as feed. This oil was also used as make-up oil in the early part of the run to supplement the process-derived oil for the recycle oil requirements. In the later part of the run, the make-up oil, if required, was made up from the accumulated process-derived oil. Run CC-15 employed filtered process derived liquids stored in Tank 4 from a recent HRI PDU run (Run 260-03) as start-up and make-up oils. Analyses of these solvents are summarized in *Table 2*.

Additives

In Run CC-7 the iron-based additive was in an oxide from. This additive was labelled as magnetic pigment and was purchased from Wright Industries (Brooklyn, New York). Analyses of the iron additive are shown in *Table 3*. In Run CC-15, iron was added as hydrated oxide and was impregnated on the coal matrix.

Liquefaction Tests

The liquefaction tests were carried out in a 20 Kg/day continuous flow unit employing two backmixed reactors, as shown *Figure 1*. An additional pretreater was added to the system in Run CC-15 for activating the iron catalyst precursor prior to the thermal stage (first stage).

Each run usually starts with coal derived distillates from Wilsonville or HRI's PDU. The unit is then brought to equilibrium by the recycling of pressure filter liquids to the coal slurry preparation section on a bi-hourly basis. Mass balance is performed every 8 or 12 hours and a daily average is then reported. Each of the conditions tested is of minimum 3 days duration to ensure the validity of the data point.

Due to the low inherent sulfur content of Black Thunder mine coal, sulfur was added in form of liquefied hydrogen sulfide to ensure proper sulfidation of the catalyst precursor as well as maintaining the supported catalyst in a sulfided state.

RESULTS AND DISCUSSION

Coal conversion is normally calculated from the ash-to-solid (quinoline insoluble) ratio of product and comparing it with the feed coal. This assumes that non-ash portion of the product is organic unconverted coal. This is not entirely true as asking transforms mineral matter into other inorganic form. In dealing with sub-bituminous coal, HRI usually considers ash on a SO_3-free basis to discount the sulfur capture by lime that might occur during asking. When additives are introduced, calculation of true coal conversion can be uncertain and imprecise. If additive contains iron as in this case, it captures sulfur from coal or coal-derived liquid or from hydrogen sulfide.

If the liquefaction product containing this sulfided iron species is ashed, the inorganic material undergoes transformation. For example, if the product contains FeS, it could be oxidized to Fe_2O_3 or some other oxide. If it is converted to Fe_2O_3, it would lose weight during asking. As a result, the amount of the mineral matter in the product would be underestimated and that of the organic matter overestimated. Calculated coal conversion would then be lower than the real conversion.

A true or more accurate value of coal conversion could be arrived at if the chemical nature of the iron species in the product and tin the ashed form is known. Since this information was lacking, it was assumed here that the iron species in the liquefaction product was present as pyrrhotite $Fe_{(1-x)}S$ with x of 0.15 and that it was converted to Fe_2O_3 during asking.

Dispersed Iron Oxide

Run CC-7 was conducted to study the effect of reactor configuration in two-stage liquefaction: catalytic/thermal vs thermal/catalytic modes of operation.

The supported catalyst charged to the unit was a blend of fresh Shell 317 catalyst (12.5 W%) and the recovered catalyst (87.5 W%) from an earlier run (CC-5). The latter was obtained from the first stage of a run which also used Black Thunder mine coal. *Table 4* summarizes the run plan and results. The catalytic stage temperature was maintained at 399 °C. The temperature of the thermal stage was varied from 440-448 °C and space velocity varied from 44-67 lb/h/ft³ cat. The additive used in this run was iron oxide, the magnetic pigment supplied by Wright Industries. The rates of the additive and hydrogen sulfide were about 5.5 and 3.8 W%.

Figure 2 and 3 compares the performance of different reactor configurations. In catalytic/thermal mode of operation, increasing the thermal stage temperature from 440 °C (Condition 1) to 448 °C (Condition 2) increased C_4-524 °C distillate yield (2.0 W% maf coal) as increased coal and residuum conversions outpaced increase in gas yield. With the thermal stage at 448 °C, catalytic/thermal configuration gave higher coal and residuum conversions relative to thermal/catalytic configuration (Condition 3). However, the product quality was superior in the latter case.

Compared to catalytic/catalytic mode (Run CC-4 Condition 2), thermal/catalytic and catalytic/thermal configurations gave slightly higher coal conversion, as shown in *Table 4*. Typically, conversion of sub-bituminous coals is quite sensitive to residence time which was less in the catalytic/catalytic mode of operation due to catalyst hold-up in the reactor. However, residuum conversion and distillate yield were higher in catalytic/catalytic configuration. The process performance in this configuration was superior with less gas yield, lighter distillate slate. Hydrogen consumption was higher, however, it was used efficiently to produce a better quality product.

Iron Impregnated Coal (CC-15)

The performance of iron impregnated (about 5000 ppm Fe) Black Thunder mine coal was measured in a thermal/catalytic mode of operation. The second stage contained

a fresh charge of Criterion 317 Ni/Mo catalyst. The catalyst was presulfided in situ by holding the catalyst at various temperature levels during the start-up period under a continuous stream of hydrogen sulfide and start-up oil.

The iron catalyst precursor(FeOOH) was activated with H_2S at 275°C (Condition 1) and 290°C (Conditions 2 to 4). The test was conducted using constant conditions of space velocity of about 42.5 lb coal/h/ft³ (supported catalyst), and temperatures of 427°C and 413°C for the thermal and the catalytic reactors, respectively. The run plan and results are given in *Table 5*.

The yield of C_1-C_3 gas remained constant around 10.5 W% maf coal reflecting the relatively stable operation. Although the results were masked by the continuous deactivation of the supported catalyst throughout the course of the run, the process performance in term of coal conversion, 524°C⁺ conversion, and C_4-524°C distillate yield were higher in tests with iron impregnated coal as compared with the untreated coal (Condition 3).

In the presence of iron additive, coal conversions varied slightly between 92.7 and 93.1 W% maf coal (Conditions 1, 2 and 4). In Condition 3, no dispersed catalyst was used. The coal conversion dropped by 2.7 W% to 90.0 W%. The decrease in residuum conversion (3.7 W%) and distillate yield (7.7 W%) were more noticeable because these performances were more sensitive to catalyst activity. Iron additive was reintroduced in Condition 4, repeat of Condition 2. The coal conversion increased back up to 92.7 W%, while the residuum conversion and distillate yield rebound to a level as projected assuming linear deactivation in catalyst activity. Interstage samples show that all coal conversion occurred in the thermal stage (at 427°C). Similar trend was observed on the effect of iron additive on coal conversion in the interstage sample, i.e. 3.7 to 4.1 W% lower when no additive was used.

The iron impregnated coal contained substantially higher nitrogen content (L-780, 2.64 W%) than the untreated coal (HRI-5828, 0.95 W%). This was probably due to the sorption of ammonium nitrate on the coal matrix during the precipitation procedure. As a result, both the interstage and the two-stage product liquids exhibited higher nitrogen content when iron impregnated coal was used, as shown in *Table 4*.

CONCLUSION

Black Thunder mine coal was liquefied in thermal/catalytic and catalytic/thermal modes of operation to study effect of iron additive on process performance. With the limited data and variations in catalyst age, in the thermal/catalytic mode of operation, it seems that the distillate yield with 5000 ppm of finely dispersed iron (on the coal matrix) was 66.0 W% and was equivalent to, if not slight more higher, than that with 5.7 W% of magnetic pigment (Run CC-7 Condition 5). However, the selectivity toward lighter product was higher in the case of magnetic pigment reflecting the higher overall reaction severity used in the test.

110

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TABLE 1
FEED COAL ANALYSES

HRI No.	5630	5828	L-780
Moisture Content, W%	6-9	8.41	8.81
Ash Content, W% (mf)	6.69	6.95	7.15
SO_3-free, W% (mf)	5.74	5.71	6.03
Ultimate Analysis, W% (maf)			
Carbon	71.90	72.51	72.38
Hydrogen	4.91	4.08	4.31
Sulfur	0.38	0.51	0.49
Nitrogen	1.04	0.95	2.64
Oxygen (by diff.)	21.77	21.95	20.18
Iron Content, W% (mf)	n/a	0.20	0.57-0.65

TABLE 2
ANALYSES OF START-UP SOLVENT

HRI No.	5648	L-769
API Gravity	n/a	10.1
Elemental Analysis, W%		
Carbon	90.14	88.95
Hydrogen	9.85	10.08
Sulfur	0.13	0.06
Nitrogen	0.37	0.34
ASTM D-1160 Distillation,		
IBP	391	318
5 V%	413	339
10 V%	426	345
20 V%	432	358
30 V%	443	366
40 V%	450	376
50 V%	459	385
60 V%	469	398
70 V%	476	416
80 V%	483	449
90 V%	499	479
95 V%	511	517
FBP	542	524*

* Boiling point at 96 V%

TABLE 3
ANALYSES OF IRON ADDITIVES

Magnetic Pigment

Moisture, W%	0.02
Sulfur, W%	0.003
Iron, W%	61.22

Forms of Iron, W%

Fe		0.05
FeO		25.14
Fe_2O_3	70.42	

TABLE 4
Evaluation of Dispersed Iron Oxide (CC-7)
Catalyst: Shell 317 Ni/Mo   Coal: Black Thunder Mine

Run No.	7	7	7	7	7	4
Condition	1	2	3	4	5	2
Mode						
1st Stage	Cat.	Cat.	Therm.	Therm.	Therm.	Cat.
2nd Stage	Therm.	Therm.	Cat.	Cat.	Cat.	Cat.
Temperature, °C						
1st Stage	398	399	448	448	441	399
2nd Stage	441	448	399	399	399	441
Catalyst Age, lb coal/lb cat.						
1st Stage	658	801	---	---	---	717
2nd Stage	---	---	974	1101	1107	1088
Space Velocity						
lb coal/h/ft_3 cat.	66.9	65.6	68.3	45.7	43.8	68.9
Addiditive Rate, W% mf coal	5.5	5.3	5.5	5.4	5.7	5.2
H_2S Rate, W% mf coal	4.5	4.7	4.3	6.3	5.4	1.8
Performance, W% maf coal						
C_1-C_3	9.96	12.01	4.81	17.41	14.10	8.81
H_2 Used	6.73	7.43	8.07	8.31	8.28	8.60
C_4-524°C	58.5	60.5	59.4	55.8	59.0	64.6
Coal Conversion	90.4	93.3	91.3	92.4	90.8	88.1
524°C+ Conv.	85.5	89.0	89.1	87.7	87.4	87.5
HDN	57.4	55.1	71.2	69.0	53.9	76.9

TABLE 5
Evaluation of FeOOH Impreganted Coal (CC-15)
Catalyst: Shell 317 Ni/Mo   Coal: Black Thunder Mine

Condition	1	2	3	4
Mode				
1st Stage	Therm.	Therm.	Therm.	Therm.
2nd Stage	Cat.	Cat.	Cat.	Cat.
Temperature, °C				
Pretreating	275	298	297	297
1st Stage	426	429	427	427
2nd Stage	413	412	413	412
Catalyst Age, lb coal/lb cat.				
2nd Stage	143	227	314	403
Space Velocity				
lb coal/h/ft$_3$ cat.	42.3	41.7	43.7	42,7
Addiditive Rate, W% mf coal	0.4	0.4	None	0.4
H$_2$S Rate, W% mf coal	3.5	3.6	3.2	3.0
Performance, W% maf coal				
C$_1$-C$_3$	10.55	10.78	10.35	10.49
H$_2$ Used	9.26	9.0	8.14	8.34
C$_4$-524°C	66.1	64.1	56.4	60.2
Coal Conversion				
1st Stage	91.1	91.1	87.0	90.7
2nd Stage	93.1	92.7	90.0	92.7
524°C$^+$ Conv.	89.1	87.7	84.0	85.3
HDN	90.0	87.1	66.6	82.6

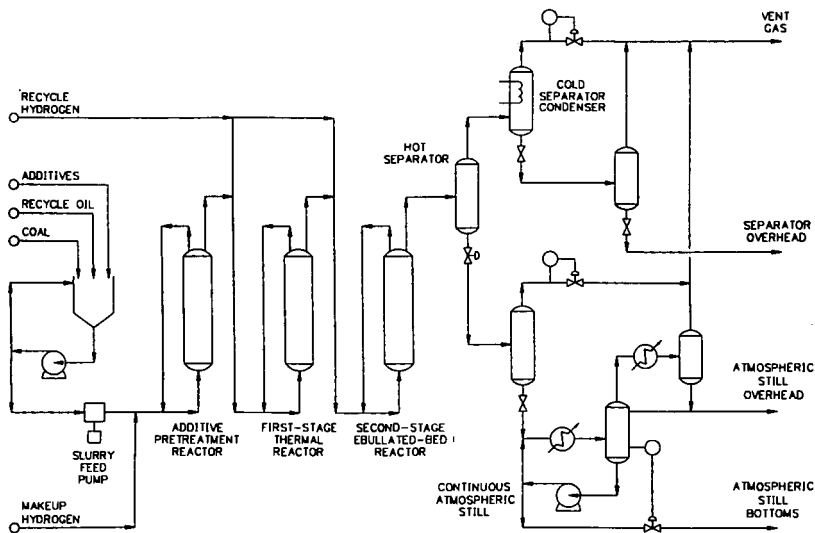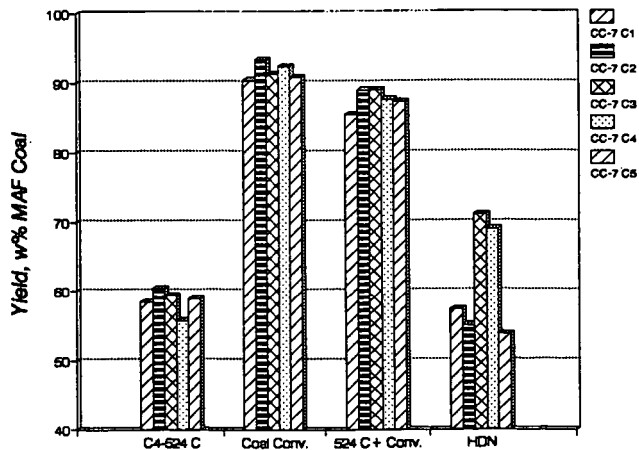**FIGURE 1 - HRI TWO STAGE EBULLATED BED BENCH SCALE UNIT**

**FIGURE 2 - PROCESS PERFORMANCE OF IRON OXIDE AS ADDITIVE:
CATALYTIC/THERMAL vs THERMAL/CATALYTIC**

FIGURE 3 - PROCESS PERFORMANCE OF IRON OXIDE AS ADDITIVE: GAS YIELD AND HYDROGEN CONSUMPTION
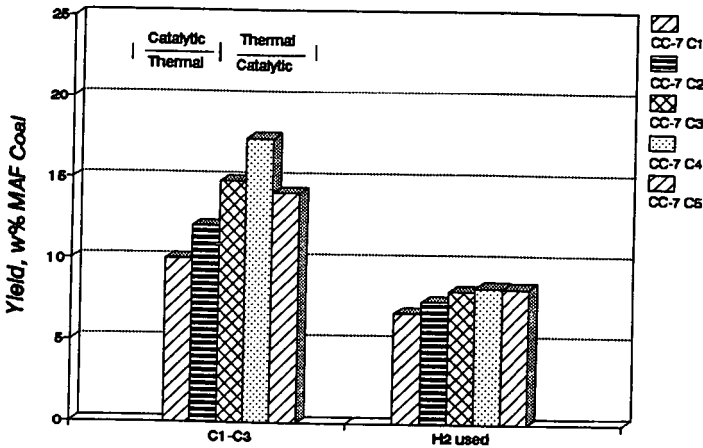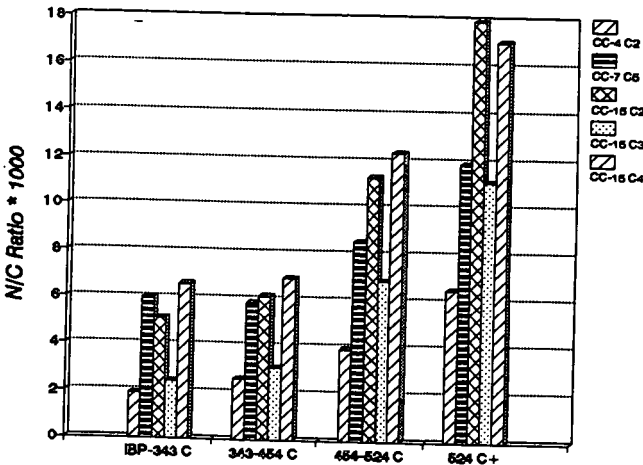

FIGURE 4 - NITROGEN CONTENT OF SELECTED INTERSTAGE SAMPLES

HYDROGENOLYTIC ACTIVITY OF SOLUBLE AND SOLID Fe-BASED CATALYSTS AS RELATED TO COAL LIQUEFACTION EFFICIENCY

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ABSTRACT

A comparative activity study of soluble and solid Fe-containing catalysts for hydrogenolysis of (1) coal-simulating compounds, i.e., 2-isopropylnaphthalene (IPN) and diphenylmethane (DPM), and (2) a Blind Canyon coal sample (designated as DECS-17), was performed. The soluble catalysts were supported on SiO_2 and included aqua complexes of various Fe salts, i.e., sulfate, acetate and chloride. The solid catalysts consisted of finely dispersed superacids, i.e., Fe_2O_3/SO_4^{2-} and ZrO_2/SO_4^{2-}. The soluble catalysts contain the aqua complex ion $[Fe(H_2O)_6]^{3+}$, which is pre-formed or formed *in situ* in the presence of water, and acts as a protonic acid by ligand dissociation especially above 250°C. Kinetic rate constants for hydrodealkylation of IPN and hydrogenolytic cleavage of DPM show that at temperatures of 350-400°C the above solid superacids possess markedly higher activity as compared with that of the SiO_2-supported, soluble Fe salts. In agreement with this finding, the same solid superacids were found to be effective hydrogenolysis catalysts in the depolymerization of the Blind Canyon coal sample. Therefore, small amounts (0.1-0.5 wt %) of Fe-containing solid superacids can be conveniently used in the initial step of a modified version of the previously developed HT-BCD (mild hydrotreatment-base catalyzed depolymerization) coal liquefaction procedure.

INTRODUCTION

An important aspect of direct coal liquefaction research is the development of effective catalysts for the chemical reactions involved in the liquefaction process. A large variety of catalysts have been investigated in fundamental studies, but two groups of catalysts have attracted particular attention, i.e.,(1) bifunctional metal sulfides which are believed to act mainly as ring hydrogenation but also as C-O, C-S, C-N, and C-C hydrogenolysis catalysts, and (2) soluble or solid acid catalysts which cause primarily hydrogenolytic bond cleavage[1].

In recent years the concept of applying disposable, highly dispersed iron-based catalysts in coal liquefaction has attracted considerable interest. The advantage of these catalysts is seen in their anticipated high activity, low cost, and environmental acceptance. Iron-based catalysts which can be added to coal in the form of very fine solid dispersions include iron oxide, iron oxyhydroxide, prepared by different methods[2,3], iron carbides[4], and others. Alternatively, coal impregnation with soluble iron compounds has been examined using various methods[5-12].

Numerous studies have been performed on a sulfated iron oxide catalyst[13-15]. An IR spectroscopic study, performed by Yamaguchi et al. [13] indicated the presence of surface

complexes between SO_4^{2-} ions and iron oxide. It was proposed that a chelated iron oxide-sulfate structure, containing two covalent $S=O$ double bonds, is responsible for the strong acidity of sulfated iron oxide. Hino and Arata used this catalyst for various acid-catalyzed reactions, e.g., dehydration of ethanol[14], and skeletal isomerization of butane to isobutane at low temperatures[15]. They pointed out that Fe_2O_3/SO_4^{2-} catalyst can be considered as a superacid.

Previous reports have shown that many iron compounds in their original form are not the active catalysts in direct coal liquefaction processes. Rather, it is assumed that such iron compounds are converted under coal liquefaction conditions, viz, in the presence of sulfur [3,16] or other sulfidation agents [17] to very active forms of non-stoichiometric pyrrohotites. The introduction of sulfate ions on the surface of iron oxide catalyst apparently enables its transformation into fine particles of pyrrohotite, which is characterized by high acidity and other properties[18].

Shabtai et al.[5-7] have recently developed a two-stage, low-temperature coal depolymerization-liquefaction procedure. In the first step of the depolymerization stage, a coal sample is impregnated with a soluble, highly dispersed iron catalyst[19] and then subjected to mild hydrotreatment (HT) at temperatures $\leq 290°C$ and a H_2 pressure of 1000-1500 psig. The mild hydrotreatment results in partial depolymerization of the coal by preferential hydrogenolytic cleavage of alkylene, benzyl etheric, cycloalkyl etheric and some activated thioetheric linkages. In the second depolymerization step, the mildly hydrotreated coal sample is subjected to base-catalyzed depolymerization (BCD) at $\leq 290°C$ with a methanolic solution of KOH or $Ca(OH)_2$. This completes the coal depolymerization by hydrolysis (alcoholysis) of diaryletheric, aryl cycloalkyl etheric, diaryl thioetheric and other bridging groups. The sequential HT-BCD treatment results in a mixture of low M.W. (about 100-300) products, composed primarily of monocluster compounds.

In the present study the hydrogenolytic activity of soluble vs solid Fe-containing catalysts was compared, using the hydrodealkylation of 2-isopropylnaphthalene and the hydrogenolysis of diphenylmethane as model reactions. In parallel, the activity of the two types of acid catalysts in the framework of the HT-BCD procedure (as measured by the overall yield of depolymerized coal products) was examined, using a Blind Canyon coal sample (DECS-17) as feed.

EXPERIMENTAL

Materials. 2-isopropylnaphthalene (purity, 98%) was obtained from Willey Organics. Diphenylmethane (purity, 99%) was obtained from Aldrich Chemical Company, and n-dodecane (purity, 99%) from Phillips Petroleum Company. Coal samples (DECS-17) were supplied by the Penn State Coal Sample Bank.

Preparation of Catalysts. Two series of catalysts were prepared.

The first series consisted of three SiO_2-supported soluble salts, i.e., $FeCl_3·6H_2O$, $Fe_2(SO_4)_3·5H_2O$ and $Fe(CH_3COO)_3$. Those were prepared by incipient wetness impregnation of SiO_2 (Aldrich,

grade 62, 60-200 mesh, 150 Å) with aqueous solutions of the respective salts, followed by drying under vacuum for 24 hours at room temperature. An alternative drying procedure, which produced a more active $Fe_2(SO_4)_3 \cdot 5H_2O/SiO_2$ catalyst involved drying of this catalyst in air at 120°C. The second series of catalysts comprised two solid superacids, i.e., Fe_2O_3/SO_4^{2-} and ZrO_2/SO_4^{2-}, which were prepared as follows:

$\underline{Fe_2O_3/SO_4^{2-}}$. A solution of 25 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ and 50 g of urea in 1000 ml of distilled water was heated at 95°C for 2 h. The precipitate formed was filtered, washed with hot water (until no free SO_4^{2-} ions could be detected) and dried at 100°C for 24 h. The dry product was treated with 0.5 M H_2SO_4 (10 ml/g of solid) with continuous stirring, and then filtered, dried at 100°C for 24 h and calcined at 500°C for 3 h.

$\underline{ZrO_2/SO_4^{2-}}$. 25 g of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 150 ml of water and subjected to hydrolysis at room temperature by slowly adding 28-30 % NH_4OH with vigorous mixing, until a pH=8.5 was reached. The precipitate was filtered, washed with distilled water until no free Cl⁻ ions could be detected, and then dried at 110°C for 24 h. The dry solid was pulverized to -100 mesh and treated with 0.5 M H_2SO_4 (10 ml/g of solid) for 1 h with continuous stirring, and then filtered, dried at 100°C for 24 h and calcined at 650°C for 3 h.

Procedure of Kinetic Hydrogenolysis Studies. The kinetic studies of model compounds, in particular 2-isopropylnaphthalene, were carried out in a 50 ml Microclave reactor (Autoclave Engineers) equipped with a special sampling device. Twenty grams of a solution containing 2 wt.% of 2-isopropylnaphthalene in n-dodecane and the catalyst were introduced in the reactor and the latter was quickly closed, purged with nitrogen and then pressurized with hydrogen to an initial pressure of 800 psig. The reactor was brought to the desired temperature (350-400°C) in 12-15 min., and at this point stirring (800 r.p.m.) was started. After each sampling, at intervals of 5-10 min., some hydrogen addition was necessary to keep a constant hydrogen pressure of 1500 psig. The reaction products were analyzed by gas chromatography using a 4 m x 0.3 cm o.d. stainless steel column packed with 10% OV-17 on Chromosorb W-HP.

The treatment of the kinetic data was made on the basis of pseudo-first-order reaction in reactant concentration, viz.,

$$-\ln(1-x_i) = kWf(t/V)$$

where k is the rate constant; x_i is the conversion at time t_i; W is the catalyst weight, and $f(t/V)$, (volume-corrected space time) is defined by

$$f(t/V) = \sum_{i=1}^{n} \frac{t_i^c - t_{i-1}^c}{V_{i-1}}$$

in which, n is the total number of intervals between the samples; V_{i-1} is the liquid volume remaining in the reactor during a given time period, and t^c is the corrected time.

RESULTS AND DISCUSSION

Table 1 summarizes the values of the pseudo-first-order kinetic rate constants (k_1) for hydrodealkylation of 2-isopropylnaphthalene, IPN (to yield naphthalene and propane) as a function of catalyst type. The Table also provides the values of the rate constants (k_2) for the competing ring hydrogenation of IPN to yield 2-isopropyl-1,2,3,4-tetrahydronaphthalene. Kinetic runs were performed at two different temperatures, i.e., 350 and 400°C (for other conditions, and for the experimental procedure, see Experimental). The k_1 values obtained were taken as a measure of the hydrogenolytic activity of the catalysts.

As seen, at 350°C the solid superacid catalysts 4 and 5 show markedly higher hydrogenolytic activity than the supported soluble catalysts 1 and 2. The difference in activity becomes larger with increase in reaction temperature to 400°C. The supported anhydrous $Fe(CH_3COO)_3$ catalyst shows the lowest activity among the soluble Fe salt catalysts. Addition of a small amount of water to this catalysts (see footnote d, Table 1) prior to reaction, resulted in some hydrogenolysis activity, which, however is lower than that of catalysts 1 and 2 which contain the pre-formed aqua complex $Fe(H_2O)_6^{3+}$. The latter has been previously indicated[20] as the precursor of active, protonic acid-generating species, e.g., $H^+[Fe(H_2O)_5OH]^-$. The relatively low activity of catalyst 3, even in the presence of water, indicates that it is preferable to use pre-formed aqua complexes of Fe salts. The thermal stability of such catalysts between 250-400°C is presently being investigated in this laboratory. The very low values of the ring hydrogenation rate constants (k_2) with the supported soluble catalysts 1-3 indicates that the latter possess essentially no ring hydrogenation activity, viz., they act as selective, monofunctional hydrogenolysis catalysts. In contrast, the Fe_2O_3/SO_4^{2-} catalyst 4 shows moderate ring hydrogenation activity, especially at 400°C ($k_2 = 0.30$). This would indicate that under reaction conditions (H_2 pressure; elevated temperature) the sulfated iron oxide may be converted to a bifunctinal catalyst system containing not only a strongly acidic functional group, but also a moderately active ring hydrogenation co-catalytic component. This could explain the overall good efficiency of this catalyst under coal liquefaction conditions.

The observed extraordinarily high hydrogenolytic activity of ZrO_2/SO_4^{2-} suggests the desirability of developing active Fe_2O_3-ZrO_2/SO_4^{2-} co-catalysts. Work on such catalyst systems is presently underway in this laboratory. Parallel hydrogenolytic activity studies with diphenylmethane (DPM) as feed showed similar trends as those in Table 1. However, the rate constants for hydrogenolytic cleavage of DPM (to yield benzene and toluene) were lower, due to the slower protonation rate of the monocyclic aromatic rings in DPM, as compared with that of the bicyclic arene system in IPN.

Table 2 summarizes the total conversions of the Blind Canyon coal sample (DECS-17) into depolymerized, THF-soluble products obtained by HT-BCD treatment, using different acid

TABLE 1. Kinetic Rate Constants for Hydrogenolysis (Hydrodelkylation) and Ring Hydrogenation of 2-Isopropylnaphthalene (IPN) as a Function of Catalyst Type[a-c].

Catalyst	$k_1 \times 10^2$ (ml/g·min), hydrodealkylation		$k_2 \times 10^2$ (ml/g·min), ring hydrogenation	
	350°C	400°C	350°C	400°C
(1) $FeCl_3.6H_2O/SiO_2$	3.9	31.5	0.2	0.7
(2) $Fe_2(SO_4)_3.5H_2O/SiO_2$	2.4	10.6	0.4	1.3
(3) $Fe(CH_3COO)_3/SiO_2$[d]	0.4	6.9	0.2	0.5
(4) Fe_2O_3/SO_4^{2-}	6.2	99.2	4.2	30.0
(5) ZrO_2/SO_4^{2-}	372.5	565.9	4.1	5.7

[a] In each kinetic run was used 20 g (26.7 ml) of a 2.0% by weight solution of IPN in n-dodecane.

[b] The amount of SiO_2-supported soluble catalysts 1, 2 and 3 used in each run was 4 g. The rate constants for these catalysts were calculated on a SiO_2-free basis. The amount of superacids 4 and 5 used in each run was 5000 ppm (0.5%).

[c] Reaction conditions: H_2 pressure, 1500 psig; temperature, 350 or 400°C; microclave reactor volume, 50 ml; sampling time intervals, 5-10 min.; total reaction time, 75 min.

[d] A calculated amount of water, needed for *in situ* formation of the $Fe(H_2O)_6^{3+}$ ion was added to this supported anhydrous salt, prior to reaction.

121

catalysts in the HT reactor (a flow reactor system was used in this part of the study). As seen, using either the soluble aqua complexes of Fe salts (unsupported; impregnated in the coal) or solid superacids (in the form of fine dispersions; physical mixture with coal) results in a very high level of depolymerization (92.4-94.5 wt.%, calculated on the pre-extracted (THF) DECS-17 sample; MAF basis). However, the impregnated aqua complexes can be applied as acid catalysts at a mild HT temperatures (275-325°C) whereas the use of finely dispersed solid superacids in the HT treatment requires temperatures of ≥ 340°C.

TABLE 2. HT-BCD Treatment of Blind Canyon Coal (DECS-17) using different acid catalysts in the HT reactor[a]

HT Catalyst	Catalyst/Feed Ratio	HT Temp., °C	HT-BCD Conversion[b]
$Fe_2(H_2O)_5(SO_4)_3$	1:9	325	92.7
$Fe(H_2O)_6Cl_3$	1:9	300	94.1
Fe_2O_3/SO_4^{2-}	1:200	340	92.4
ZrO_2/SO_4^{2-}	1:200	340	94.5

[a] In each run was used 10.0 g of coal-catalyst mixture. HT reaction conditions: H_2 pressure, 1500 psig; H_2 flow rate, 50 sccm; total reaction time, 2 h. BCD reaction conditions: catalyst-solvent system, 10% KOH solution in MeOH; temperature, 290°C; total reaction time, 1 h.

[b] Total yield of THF solubles (MAF basis), calculated on the pre-extracted Blind Canyon coal feed.

CONCLUSIONS

1. Kinetic studies of acid-catalysed hydrogenolysis of 2-isopropylnaphthalene and diphenylmethane show that (in the temperature range of 350-400°C) finely dispersed solid superacids, e.g., Fe_2O_3/SO_4^{2-} and ZrO_2/SO_4^{2-}, possess markedly higher hydrogenolytic activity as compared with that of soluble aqua complexes of Fe salts, e.g., Fe sulfate, chloride and acetate (supported on SiO_2).

2. In agreement with the above, it is found that solid superacids, in very low concentrations (0.1-0.5 wt.%) can be conveniently applied as hydrogenolysis catalysts in the HT step of the HT-BCD coal depolymerization process[5-7]. The effective application of superacid catalysts in this process, however, requires HT temperatures ≥ 340°C, which are considerably higher than those found as optimal in the case of impregnated soluble Fe salts as hydrogenolysis catalysts (275-300°C).

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IRON CATALYSTS IN COAL HYDROGENATION

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ABSTRACT

Hydrogenation of a set of low and high rank coals was studied using iron containing species as catalyst. Three catalytic precursors were used: $FeSO_4 \cdot 7H_2O$ (IS), Fe_2O_3 (RM) and $Fe(CO)_5$ (IP). The addition of catalyst increased the conversion in important extent when low rank coals were hydrogenated and in a more moderate way with the bitumminous coals under an initial hydrogen pressure of 10 MPa and in absence of solvent, dry hydrogenation. When CS_2 was added to high sulphur content coals only slight increase of oils formation was observed. However, significative higher conversions to asphaltenes and oils were reached when the coal sulphur content was around 1 %. It seems to be more important the amount of total sulphur than its organic or inorganic nature.

INTRODUCTION

Coal hydrogenation processes consists in coal transformation into progressively lighter products in order to obtain oil. In general, the product distribution of processes such as hydroliquefaction and hydropyrolysis, shows a mixture of low-molecular weight oils, asphaltenes and preasphaltenes, as well as the insoluble residue. The hydrogenation has been widely used, not only for its interest in hydrocarbon production, but also as an strategy of degradative reaction applied to coal in order to study the coal structure.

Both approaches to coal, the practical and the theorical one, seem to be nowadays not yet resolved, regardless the great research effort that is been done, in many senses, process development, variables optimization and catalyst selection.

Iron containing compounds have been widely studied as hydrogenation catalysts, due to their relatively low cost, hydrogenation activity and iron descarboxilation potential. Several ways of iron addition to the coal can be used. Each one presents advantages and drawbacks. The iron precursors dispersion onto the coal surface is now generally considered to have a beneficial effects, that increases the amount of active catalyst surface area available at the same loads. This dispersion requires the previous dissolution of the precursors and several of the compounds of interest as liquefaction catalysts, such pyrite, iron oxide, are insoluble in common solvents. Other solid precursors have to be added by physical mixing. The organometallic species are usually added with the hydrogenation solvent; when the working procedure is dry, liquid species as $Fe(CO)_5$ can be just added to the coal previously to the introduction into the reactor. In all the cases, the active form of the iron catalyst is considered to be the iron sulphide.

The aim of this work is to study the effect of the hydrogenation temperature and catalysts on the product distribution and characteristics, when the hydrogenation is carried out in absence of solvent, keeping constants the initial hydrogen pressure and the hydrogenation time.

EXPERIMENTAL

The work reported is part of a broader investigation (1) of dry catalytic hydrogenation of a set of 25 coals from different mining areas around the world. For this paper, the results

obtained with 9 of these coals, 6 from Spain (Ref. S9, S13, S16, S18, S20 and B23), one from USA (Illinois No 6,Ref. B19), one from Germany (Zollverein,Ref. B22) and one from UK (Bagworth,Ref. B25). The low-rank coals are from Mequinenza (S9), Andorra-Ariño (S13, S16 and S18) and Portalrubio (S20) and were selected as a function of their nature(2). The analysis of the coals are compilated in Table 1.

Catalyst Precursors

Three iron containing precursors with iron in different oxidation stages were used: $FeSO_4.7H_2O$, Red Mud (36.5% Fe_2O_3) and $Fe(CO)_5$. The first one was converted "in situ" into iron sulphide by H_2S bubbling for 30 min through the alkaline aqueous solution. Then was dispersed on coal using coal as catalytic support. The two others precursors were added to coal before hydrogenation by direct physical mixing (RM) or by embedding ($Fe(CO)_5$). The catalyst loading was equivalent to 5% wt iron of dmmf coal.

Hydrogenation Procedure

The hydrogenation was carried out in small reactors type tubing bomb (160cc capacity) loaded with about 10 g of daf coal and catalyst, pressurized with H_2 to 10 MPa and heated in a fluidized sand bath for 30 min at 300, 350, 400, 425, 450 and 500°C. When the coal sulphur content was low, CS_2 was added.

The products work-up was according to Fig 1. The gas were analyzed by GC, the oils by elemental analysis, FTIR, TLC-FID and simulated distillation by GC. The THF-insolubles by CP-MAS 13C nmr and FTIR

RESULTS AND DISCUSSION

As the numerical data on conversions and derived product distributions of each coal would enlarge this paper, tables 2 and 3 show the results obtained with coals Ref. S13 and B25 as representative models. However, comments on the other hydrogenated coals will be done along this paper since each coal has its own characteristics.

The selected coals, apart from low and high rank coals can be classified as high and low sulphur content coals. The percentages are calculated on "as received" basis. While the low rank coals have %S ranging from 8.6% to 5.7%, the bituminous coals show a total sulphur content around 1%, with the exception to B19 with 3.9% of total sulphur. That is the reason why to very few experiments has been added CS_2, see Table 2, when S13 coal has been hydrogenated. Coals S13, S16, and S20 have about the same organic sulphur contents (4%), while S18 has more pyritic sulphur (3.80%) and S9 has much more organic sulphur (7.78%). Not one of these coals need CS_2 addition to reach high conversions in iron catalytic hydrogenation and when CS_2 was added not significative variations were detected on conversion percentages nor THF-solubles; only a very slight increase in oils formation percentages were obtained.

Keeping constants the hydrogenation time and the starting hydrogen pressure, in general, the higher the temperature, the higher the conversions, the THF-solubles and the oils percentages.

The very high conversions (95% dmmf for the S9 coal) reached with these low-rank high-sulphur content coals seem to show that it does not matter the origin of the sulphur, organic or inorganic, the real point seems to be the total amount of sulphur present in order to reach the H_2S pressure to convert the iron (whatever be its original oxidation degree) from the catalytic precursor into the iron sulphide salt which is the active form (3). On the other side the SEM analysis shows that if the H_2S pressure is sufficient at the end of the processes most of the iron is in the sulphide form. The optical microscopy shows the superficial, not yet the nucleous, transformation of the pyrite nodules from the inherent mineral matter into pyrrhotite on the THF-insolubles from non-catalyzed test at 300 °C. This

transformation is complete at 350 °C.

The presence of iron catalyst increased coal conversion from 47% to 75% (IS), 60% (RM) and 59% (IP) at 350 °C and from 76% to 89% (IS), 95% (RM) and 91% (IC) at 400°C when S9 coal was hydrogenated. With the bituminous coals the different between non-catalytic and catalytic processes was not so pronounced, but significative enlargement were reached when CS_2 was added.

For the B22, B23, and B25, Table 3, at the lowest temperature studied, the addition of CS_2 is not determinant because at this temperature there are not yet thermic nor catalytic cracking with these high rank coals, but at the medium temperatures studied, 350°C and 400°C, the CS_2 addition influences helping to stabilize the radicals from both thermic and catalytic cracking. The bituminous coal with an intermediate total sulphur content (B19) follows the some trends but the effect of CS_2 addition is significative in a minor extent.

The nature of the oils, analyzed by TLC-FID, show to be mainly aromatic and polar, with percentages in saturate compounds always minor to 3% . On polar percentages, the nature of the iron precursor is not relevant but the increase of the process temperature means a reduction of polars to the corresponding aromatic compounds.

The curves of simulated distillation, from the oils by GC analysis, show that there are not conversion into light fractions with low-molecular weight, the gas oil fraction is very scare, always lower than 2% and the rest of the components are heavy oils.

The transformation of coal into liquids has been followed by solid state nmr spectroscopy of the THF insolubles, Tables 5 and 6. Due to the magnetic properties of this analytical technic and to the iron catalysts used, in some of the spectra was not easy the chemical shift assignation, so only the aliphatic (0-100 ppm) and aromatic (100-190 ppm) carbons have been assigned. These troubles were deeper when RM than when $FeSO_4$ was used. In order to do not lose rigor, the simplification was done in all the cases. It can be deduced a gradual diminution in the length of the alkylic chains and with increasing hydrogenation temperature, an increasing aromaticity slightly higher when red mud is the catalytic precursor. The FTIR (Fig. 2), confirms the disapperance of aliphatic chains, the decrease in oxygen groups and the aromaticity increase.

Summarizing, at the conditions studied, it can be concluded: a) The importance of the total amount of sulphur in order to reach the suitable H_2S pressure, being not significative the organic or inorganic nature of the parent sulphur. b) The CS_2 addition does not influence the yields from high-sulphur content coals, but increases conversions and THF-solubles, mainly asphaltenes formation, when about 1 % is the inherent sulphur content of coals. c) The iron of the catalytic precursor is converted into pyrrhotite in a higgher extension when it comes from IS than from RM.

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Figure 2. FT-IR spectra of THF-insolubles of B25 coal hydrogenation and raw coal.

Figure 1. Diagram of the process.

127

Table 2. Conversions and product yields (daf) from
S13 coal (10MPa H2 cold and 30 min).

Cat.	Tem. °C	CS2	% Conv	%THF sol.	O/A	%Gas formation COx	C1-C4	SH2
-	350	-	32.4	23.4	0.1	69	4	27
-	350	YES	37.7	26.9	0.2	71	5	25
-	450	-	80.5	56.3	0.4	46	18	37
IS	300	-	15.8	9.1	0.4	98	0	2
IS	350	-	82.0	69.6	0.1	78	6	16
IS	400	-	78.7	54.2	0.5	54	16	29
IS	425	-	80.2	48.9	0.7			
IS	450	-	84.8	51.2	1.1	45	41	14
RM	300	-	12.1	8.6	0.5	100	0	0
RM	350	-	33.1	23.2	0.3	86	8	5
RM	350	YES	35.6	23.9	0.4	79	8	14
RM	400	-	87.9	60.9	0.4	57	20	23
RM	425	-	84.4	53.5	0.4			
RM	450	-	64.7	30.9	0.8	50	39	11
IP	350	-	34.4	26.0	0.2	83	3	14
IP	350	YES	61.3	40.2	0.2	85	4	11
IP	400	-	75.8	50.9	0.2	69	20	12

Table 3. Conversion and product yields (daf) from
B25 coal (10MPa H2 cold and 30 min).

Cat.	Tem. °C	CS2	% Con.	%THF sol.	O/A	%Gas formation COx	C1-C4	SH2
-	350	-	14.2	8.3	0.8	77	7	14
-	400	-	39.2	32.5	0.4	51	36	13
-	450	-	40.4	22.5	1.1	41	54	5
IS	300	-	11.3	9.2	0.3	97	0	3
IS	350	-	21.3	17.3	0.2	96	0	4
IS	400	-	70.7	55.9	0.4	56	37	7
IS	425	-	79.1	58.1	0.5	43	50	7
IS	450	-	71.7	45.8	1.3	38	59	3
IS	500	-	74.1	32.0	1.3	23	73	4
RM	300	-	5.5	9.3	0.5	100	0	0
RM	300	YES	3.6	10.5	0.3	49	1	50
RM	350	-	14.7	13.3	0.3	92	8	0
RM	350	YES	19.2	19.7	0.3	48	10	43
RM	400	-	43.9	37.9	0.4	67	31	1
RM	400	YES	69.5	60.5	0.3	45	20	34
RM	425	-	73.9	55.6	0.4	50	49	1
RM	425	YES	75.1	59.8	0.6	29	28	43
RM	450	YES	70.2	44.2	0.8	24	36	40
RM	500	YES	64.6	32.8	1.4	22	72	6
IP	350	-	12.6	12.4	0.6	98	2	0
IP	350	YES	9.2	17.1	0.4	90	3	7
IP	400	YES	71.9	61.3	0.4	60	14	25
IP	450	YES	73.7	35.8	0.8	55	33	12

Table 1. Analysis of the parent coals.

Coal Ref.	C/H	Proximate analysis (%) Moist.	Ash	%MM	Volat.	C fix.	Ultimate analysis (%) C	H	N	S tot	Macerales (%vol) Vitrin.	Exin.	Inert.
S 9	0.68	11.03	21.35	27.65	36.48	31.14	44.15	5.39	0.39	8.65	90.9	0.4	8.7
S 13	0.74	17.04	11.29	19.48	29.53	42.14	48.34	5.47	0.29	6.00	71.8	3.1	25.1
S 16	0.81	12.94	11.10	18.81	29.51	46.15	49.24	5.07	0.49	6.38	74.7	1.6	23.7
S 18	0.92	12.04	15.11	24.20	29.07	43.78	49.10	4.99	0.35	6.33	75.4	1.0	23.6
S 20	1.07	9.30	38.60	58.06	22.15	29.95	38.18	2.95	0.39	5.71	62.7	1.3	36.0
B 19	1.14	3.30	13.34	17.20	31.59	31.78	64.17	4.67	1.21	3.92	89.1	1.7	9.2
B 22	1.33	1.10	12.07	12.08	25.88	60.95	72.33	4.52	1.49	0.98	67.0	9.0	19.0
B 23	1.58	0.80	8.30	11.43	16.95	74.27	82.23	4.35	1.67	1.20	92.9	0.0	7.1
B 25	1.24	13.70	7.60	11.39	34.10	44.60	62.49	4.19	1.06	1.06	72.0	5.0	23.0

Table 4. Oils nature as a function of the hydrogenation variables (10 MPa H2, cold and 30 min).

	Variables		Oil Composition (%)		
Coal	Cat.	Tem.(°C)	Sat.	Arom.	Polars
S13	-	350	1.9	56.0	42.1
S13	-	400	1.5	68.4	30.1
S13	IS	300	2.0	39.5	58.5
S13	IS	350	2.0	56.0	42.0
S13	IS	400	1.4	67.6	31.3
S13	RM	300	2.0	39.5	58.5
S13	RM	350	2.2	49.4	48.5
S13	RM	400	1.4	60.7	37.9
B25	-	350	2.4	46.9	52.0
B25	-	400	5.9	60.9	36.4
B25	IS	300	2.1	45.4	52.5
B25	IS	350	2.2	48.5	49.3
B25	IS	400	2.5	57.3	40.3
B25	IS	425	2.5	57.3	40.3
B25	RM	300	2.8	29.0	68.3
B25	RM	350	2.4	46.0	51.7
B25	RM	400	2.6	58.4	38.3
B25	RM	450	1.7	55.5	42.8

Table 5. Aromaticity and functional groups by CP-MAS C13 nmr of S13 THF-insolubles.

Chemical Shift(ppm)	Raw Coal	Blank runs		S13 IS			S13 RM		
		300°C	350°C	300°C	350°C	400°C	300°C	350°C	400°C
0 - 100	33.0	25.5	21.4	53.0	26.4	22.0	68.0	35.5	24.6
100 - 190	67.0	74.8	81.1	139.0	135.0	131.0	135.5	155.0	157.0
Aromaticity	0.66	0.71	0.78	0.71	0.82	0.85	0.67	0.78	0.84

Table 6. Aromaticity and functional groups by CP-MAS C13 nmr of B25 THF-insolubles.

Chemical Shift(ppm)	Raw Coal	B25 IS			B25 RM				
		300°C	400°C	500°C	300°C	350°C	400°C	425°C	500°C
0 - 100	33.0	35.8	15.5	7.3	34.8	26.8	11.8	12.2	4.1
100 - 190	72.0	62.9	84.3	92.7	65.2	73.2	88.2	87.8	95.9
Aromaticity	0.66	0.64	0.84	0.92	0.65	0.73	0.88	0.88	0.96

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IRON BASED CATALYSTS FOR COAL/WASTE OIL PROCESSING

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ABSTRACT
Iron based catalysts are being used in our laboratory to process coal with waste oil. Almost 1.2 billion gallons of waste oil are generated in the United States each year, posing an environmental hazard due to metal bearing compounds and high sulfur content. Waste oil is primarily paraffinic and is a poor hydrogen solvent, but contains surfactants which could help in better dispersion of the coal particles and the catalyst during liquefaction. The undissolved coal can act as a trap for the metals removed from the waste oil without significantly altering the metal content of the coal. The initial results - coal conversion over 70% and oil yield greater than 48% indicate that coprocessing coal with waste oil is beneficial. The results are preliminary and responses in coal conversion and selectivity due to different ratios of waste oil and conventional hydrogen solvents are being evaluated. The effect of various parameters such as temperature, pressure and the amount of catalyst on coal conversion and selectivity during coprocessing is being evaluated.

INTRODUCTION
The coprocessing of coal with used oil has the potential to improve the economics of coal liquefaction. Almost 1.2 billion gallons of waste oil are generated in the United States each year, posing an environmental hazard due to metal bearing compounds and high sulfur content. The used oil must be re-refined and hydrotreated before use as a fuel or as a lube base stock. The reactions during the hydrotreatment of used oil include hydrodesulfurization (HDS), hydrodemetallation (HDM) and hydrodeoxygenation (HDO). The undissolved coal during coprocessing could act as a trap for the metals removed from the oil and the sulfur present in the oil could serve to produce the sulfided catalyst needed for liquefaction. The overall objective of this work is to evaluate the beneficial effects of coprocessing coal with waste oil using iron based catalysts.

The use of unsupported dispersed catalysts for conversion of coal to liquids via direct coal liquefaction is believed to be a very effective method to overcome the limitations of supported metal catalysts [1]. The restricted access to the reaction surface of the supported metal catalysts such as CoMo/Al₂O, used in direct coal liquefaction prevents them from influencing the reactions of coal and high molecular weight coal derived products. In addition, supported metal catalysts suffer from rapid deactivation. Unsupported dispersed catalysts provide efficient contact of coal/solvent slurries with the catalyst surface [1]. The effective dispersion of the catalysts can be achieved by different methods such as using water soluble [2] or oil soluble precursors [3] and by using finely divided powders [4]. These techniques allow formation of the active inorganic phase under reaction conditions. The addition of finely divided solid precursors with high specific surface area is considered a very effective way to achieve good dispersion and improved overall coal conversion and selectivity to oil production in direct coal liquefaction [4,5].

Iron based catalysts have the potential to be used as effective dispersed catalysts and have been employed recently for direct coal liquefaction. Iron based catalysts are cheap, readily available and disposable. Sulfated iron oxide was found to be an effective catalyst for liquefaction with 86 wt% conversion and 50 wt% selectivity for oils [6]. The addition of elemental sulfur to the catalyst was found to further increase the conversion and selectivity. It was postulated that the sulfate group inhibits agglomeration of the metal oxides and subsequently increases the surface area and catalyst dispersion [6]. Oil soluble iron carbonyls have been used in direct coal liquefaction and in coprocessing with heavy oil in a number of studies [3,7-10]. The iron carbonyls are distributed throughout the coal/solvent mixture and decompose upon heating to form very small effective catalyst particles active for liquefaction of coal. The addition of sulfur in either elemental form or as an organic sulfur compound favored the formation of pyrrhotite whereas the less active iron oxide (Fe_3O_4) was formed in its absence [8]. The iron pentacarbonyl precursor was converted to pyrrhotite at the reaction conditions with time. The use of 0.5 wt% iron as iron pentacarbonyl increased the coal conversion from 39% to 82% [3]. Hematite (Fe_2O_3) was found to be a very good sulfur scavenger during coal desulfurization [11]. The iron oxide reacts with all the hydrogen sulfide released to form pyrrhotites and prevents any reaction of hydrogen sulfide with the organic constituents of the process solvent. The formation of pyrrhotites as the major phase has also been reported when iron oxide was presulfided in a mixture of hydrogen and hydrogen sulfide under reaction conditions [12].

Waste oil is primarily paraffinic and is a poor hydrogen donor solvent. It does, however, contain surfactants which could be advantageous to liquefaction. The additives found in the waste oil such as detergent/dispersant additives, oxidation inhibitors, etc., are organic sulfur compounds [13]. These additives could help effectively disperse the coal and the catalyst precursors throughout the coal/oil slurry during coprocessing. In addition, these additives can serve as sulfur sources to convert the catalyst precursors to the more active form. The unconverted coal could act as a trap for the metals removed from the oil. This has been the case during coprocessing of coal with a heavy oil where metallic impurities in the oil were found to deposit on the coal residue or pitch [14]. The demetallation of used oil during hydrotreatment was found to be primarily due to the process of physical deposition on the catalyst bed [15].

EXPERIMENTAL
The co-processing reactions in the tubing bomb were carried out using DECS 6 coal, waste oil (1% sulfur, 0.45% ash), tetralin as a solvent (in some cases), and superfine iron oxide (Fe_2O_3) as a catalyst precursor. The coal was crushed and separated to obtain a particle size of less than 16 mesh. The liquid and solid reactants were then charged in the desired proportions into a tubing bomb reactor. High pressure hydrogen was added through a fine metering valve and capped with a Swagelok fitting. The bomb was leak tested by submerging it in water. The bomb was then attached to a variable-speed motor via an extension arm. The bomb was then lowered into a fluidized sand bath to maintain the reaction temperature and was shaken vertically. At the end of the desired reaction time, the motor was stopped and the tubing bomb was removed from it. The reaction was then quenched using water at room temperature. The liquid and solid reactant mixture was filtered under vacuum to separate the solid and liquid components. The liquid portion was saved for sulfur and ash analysis. The bomb and the solids collected

in the first filter were then washed with hexane to obtain the hexane-soluble fraction. The solids remaining after hexane washing were allowed to dry before weighing. The solids were then washed with tetrahydrofuran (THF) to obtain the THF solubles. This solid was also allowed to dry before being weighed. The liquid obtained from the first filter was then tested for sulfur content using a LECO sulfur determinator (SC-32) and ash content was determined using a SYBROM Thermolyte furnace.

RESULTS AND DISCUSSION
The coal conversion during coprocessing with waste oil was defined as

Conversion = 100 * (1-X) where,

$$X = \frac{W_R - W_C - W_{ash}}{W_{ash\ free\ coal}}$$

W_R weight of residue remaining after THF wash,
W_C weight of catalyst (it was assumed that all the iron oxide was converted to FeS)
W_{ash} weight of ash in the coal

The results from coprocessing experiments are given in Table 1 (using superfine iron oxide) & Table 2 (using Fisher grade iron oxide).

The reduction in sulfur and ash are for the oil obtained after the first filter on the basis of initial analysis of waste oil. The conversion and the oil yield are very high (88% and 69% respectively) even when only coal and oil are used. The conversion increased when either tetralin or catalyst precursor (iron oxide) was added to the reaction mixture. The oil yield remained nearly same. However, both the conversion and oil yield decreased when both tetralin and iron oxide were added. The reason for this behavior is not very clear at this time and additional experiments are being conducted for confirmation. The amount of iron oxide used in these runs was the stoichiometric amount (2.5 wt% based on the oil) needed to remove all the sulfur in the waste oil. However, when the iron oxide was used in excess (1.5 times the stoichiometric amount), and the amount of tetralin was increased, the conversion and the oil yield increased as expected (89% and 48% respectively).

The reduction in the sulfur content was greater when tetralin was present in the system. This is probably due to the increased availability of hydrogen in the liquid phase when tetralin is present, leading to increased removal of sulfur by forming hydrogen sulfide. The reduction in the ash content was greater than 70% in most of the runs. The ash reduction is believed to be primarily due to the deposition of the metals on unreacted coal and residue [14,15].

CONCLUSIONS
Coprocessing coal with waste materials such as waste oil which have expensive disposal costs offers several advantages. Unsupported dispersed catalyst precursors (iron oxide) were used in an initial study to coprocess waste oil with coal. The conversion of the coal

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and the selectivity for the oil was in excess of 70% for most of the runs. The conversion and the selectivity were higher even when the catalyst precursor was not used. The sulfur and the ash content in the oil were reduced substantially during coprocessing. A detailed study is underway at present to evaluate the effect of various parameters such as different ratios of oil to hydrogen donor solvents, temperature, pressure, catalyst loading, etc., on the coal conversion and selectivity.

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Table 1.
Coprocessing Coal with Waste Oil

CATALYST* (wt%)	TETRALIN+ (wt%)	TIME (min)	CONVERSION" (%)	OIL YIELD@ (wt%)	SULFUR REDUCTION (%)	ASH REDUCTION (%)
6 grams of oil, 0.6 grams of DECS 6 coal						
-	-	60	87.84	69.27	35.80	84.10
2.50	-	60	96.13	65.64	28.85	89.06
-	20	60	93.03	70.39	38.30	72.22
2.50	20	60	71.48	36.27	40.40	-
3.75	60	30	88.93	47.68	54.90	90.67
9 grams of oil, 0.9 grams of DECS 6 coal						
-	-	30	88.96	80.37	27.00	80.02
-	-	60	71.50	71.77	27.20	73.27
-	-	90	88.87	87.12	-	38.22
2.5	20	60	91.88	35.31	40.80	75.82

* catalyst precursor: superfine iron oxide (Fe_2O_3).
+ based on amount of oil.
# tetrahydrofuran (THF) soluble MAF basis.
@ oil yield on basis of coal converted.

Reaction conditions: 400 °C, 1200 psig (at room temperature).

Table 2.
COPROCESSING COAL WITH WASTE OIL

WASTE OIL (gms)	TETRALIN (gms)	TEMPERATURE (°C)	OIL ANALYSIS*		OIL YIELD** (MAF)
			SULFUR REDUCTION (%)	ASH REDUCTION (%)	
20	-	410	30	80	55%
20	-	430	40	65	55%
10.14	10.53	430	40	85	75%

Reaction Conditions: Blind Canyon (DECS 6) coal: 2 gms; Fe_2O_3 (Fisher grade): 0.75gms. 1000 psig hydrogen pressure (at room temperature)

* Initial Analysis: Sulfur 1.01%; Ash content: 0.43%

** based on initial coal charge